

# PRIMARY ACOUSTIC THERMOMETRY FROM 217 K TO 303 K

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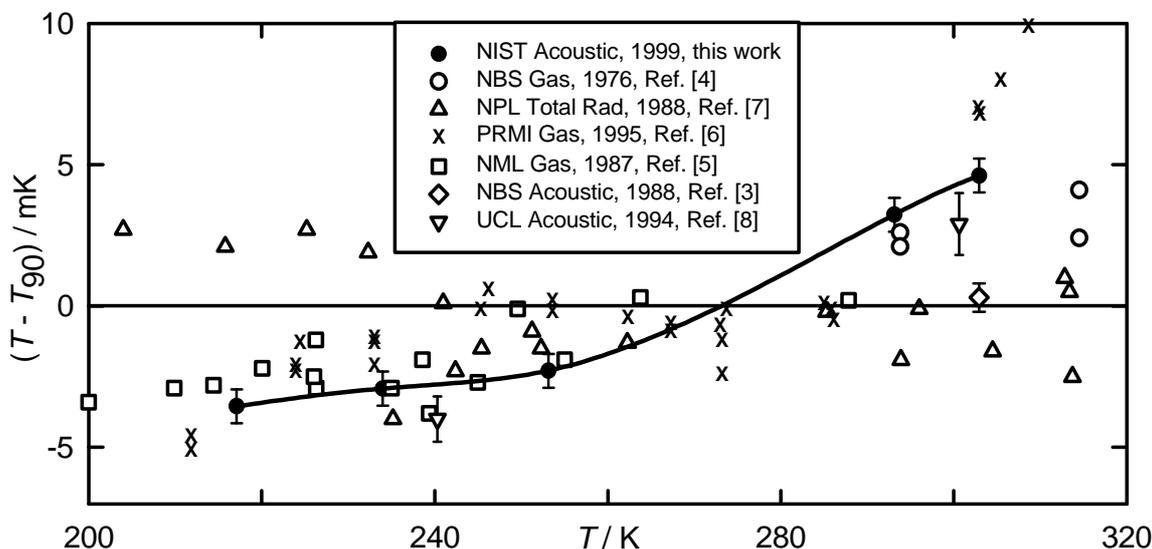
## ABSTRACT

We report new values for the difference  $(T - T_{90})$  between Kelvin thermodynamic temperatures  $T$  and ITS-90, the International Temperature Scale of 1990. The new data span the range 217 K  $\leq T \leq$  303 K with standard uncertainties of 0.6 mK. A detailed description of the measurements and their analysis is in press [1]. The new values of  $(T - T_{90})$  were obtained by measuring the speed-of-sound in argon contained in the same spherical acoustic resonator that had been used at NBS to redetermine the universal gas constant  $R$  [2]. The largest component of the uncertainty resulted from choosing among models to extrapolate the speed-of-sound data to zero pressure. At the triple point of mercury,  $(T_m - T_{90}) = (-2.3 \pm 0.6)$  mK; at the triple point of gallium,  $(T_g - T_{90}) = (4.6 \pm 0.6)$  mK. The new value of  $T_g$  is  $(4.3 \pm 0.8)$  mK larger than previously obtained with this apparatus [3]. We suspect that the earlier value of  $T_g$  is erroneous because a virtual leak at  $T_g$  progressively contaminated the argon used in that work. This suggestion is supported by new acoustic data taken when the resonator was filled with xenon. Fortunately, the virtual leak did not affect the redetermination of  $R$  [1,2]. The present work resulted in many suggestions for improving primary acoustic thermometry to achieve sub-millikelvin uncertainties over a wide temperature range.

## 1. RESULTS

In this short report, we present in order: the results, our approach for using a spherical acoustic resonator as a primary thermometer, a description of the measurements and their analysis, and a discussion of the virtual leak encountered upon replacing the argon with xenon. We conclude by listing "lessons learned" for improving primary acoustic thermometry.

Figure 1. Comparison of the Kelvin thermodynamic temperature scale and ITS-90.



On Fig. 1, the non-acoustic data [4,5,6,7], except the 1995 PRMI corrected results [8], were used to establish ITS-90. The data at 240 K and 300 K labeled "UCL Acoustic, 1994, Ref. [8]" are unpublished primary acoustic thermometry results from University College London that agree with the present results within the remarkably small combined uncertainties. After being corrected in 1995, the PRMI gas thermometry results also agree very well with the present results [6]. (Before correction, the PRMI results were close to the  $T_{90}$  baseline.) In summary, the results obtained since 1990 suggest that ITS-90 can be improved.

In Fig. 1, the datum at  $T_g = 302$  K labeled "NBS Acoustic, 1988, Ref [3]" was also obtained with the gas-constant resonator. It differs from the present value by  $(4.3 \pm 0.8)$  mK, an amount that is much larger than the combined instrumental uncertainties. We conjecture that this 1988 value was erroneous because a virtual leak contaminated the argon used in their work. Below, Section 5 presents evidence supporting this conjecture.

## 2. PRIMARY ACOUSTIC THERMOMETRY WITH A SPHERICAL RESONATOR

Primary acoustic thermometry relies on the connection between the speed of sound in a gas and the thermodynamic temperature of that gas. Hydrodynamics and the kinetic theory of dilute gases relate the thermodynamic temperature  $T$ , the average kinetic energy  $E$  in one degree of freedom, and the speed of sound  $u$ . In the simplest approximation

$$3E = \frac{1}{2} m v_{\text{rms}}^2 = \frac{3}{2} k_B T, \quad u^2 = \frac{C_p}{C_v} v_{\text{rms}}^2. \quad (1)$$

Here,  $v_{\text{rms}}$  is the root mean square speed of a gas molecule,  $m$  is its mass,  $k_B$  is the Boltzmann constant, and  $C_p/C_v$  is the ratio of the constant pressure to constant volume heat capacities. For monatomic gases,  $C_p/C_v = 5/3$  as p60. The International System of Units assigns the exact value 273.16 K to the temperature of the triple point of water  $T_w$ . From this assignment and from Eq. (1), the Kelvin thermodynamic temperature  $T$  of a gas can be determined from the zero-pressure limit of the ratio of speed of sound measurements at  $T$  and  $T_w$  using the equation

$$\frac{T}{273.16 \text{ K}} = \lim_{p \rightarrow 0} \left( \frac{u^2(p, T)}{u^2(p, T_w)} \right). \quad (2)$$

In the present work, the speed-of-sound ratios were determined using the spherical, stainless-steel shell that had been used to acoustically redetermine the universal gas constant  $R$ . This shell had a 1 cm-thick wall bounding a spherical cavity with a radius of 9 cm. We measured the frequencies  $f_m(T)$  of the microwave resonances of the cavity while it was evacuated. The microwave frequencies were used to deduce the thermal expansion of the cavity. We also measured, as a function of the temperature and the pressure, the resonance frequencies  $f_a(p, T)$  of the radially symmetric acoustic modes of the cavity while it was filled with argon. To deduce  $u^2(p, T)$ , the acoustic frequencies were combined with the volume of the resonator at  $T_w$  from Ref. [2] and the thermal expansion deduced from  $f_m(T)$ . To obtain zero-pressure ratios of  $u^2(p, T)/u^2(p, T_w)$ , the values of  $u^2(p, T)$  were fitted by theoretically-motivated functions.

The radially symmetric acoustic modes are non-degenerate for a perfect sphere and they were well-separated from other modes in the imperfect gas-constant resonator used here. In contrast, the non-radially symmetric modes were split into partially overlapping multiplets. If they had been used, the determination of  $f_a(p, T)$  would have been much more complicated and the results would have had much larger uncertainties.

The Kelvin thermodynamic temperature is determined, approximately from the measured quantities by

$$\frac{T}{273.16 \text{ K}} = \lim_{p \rightarrow 0} \left( \frac{f_a(p, T) \% f_a(p, T)}{f_a(p, T_w) \% f_a(p, T_w)} \right)^2 \times \left( \frac{\langle f_m(T_w) \% \rangle f_m(T_w)}{\langle f_m(T) \% \rangle f_m(T)} \right)^2. \quad (3)$$

Because there are no radially symmetric microwave modes, it was necessary to use appropriately weighted averages of the microwave frequencies  $f_m(T)$ ; this is indicated by the brackets " $\langle \dots \rangle$ " in Eq. (3). [9] (Partially resolved triplets of microwave modes were used.) In Eq. (3), the terms  $f_a(p, T)$  and  $f_m(T)$  represent small corrections that must be applied to the acoustic and microwave frequencies, respectively. These corrections depend upon auxiliary data including the thermal conductivity of the argon, the electrical resistivity of the stainless-steel shell, and the mechanical response of the shell to the acoustic pressure.

Eq. (3) implicitly assumes that the same acoustic and microwave modes were used for the frequency measurements at  $T$  and at  $T_w$  and that the same gas was used for the acoustic measurements at both temperatures. Maintaining the purity of the argon was a major concern and this is considered in Section 5.

As implied by the absence of resonator's dimensions and eigenvalues in Eq. (3) and as emphasized by Mehl and Moldover [10], the spherical cavity plays a limited role in measuring  $u/c$ , the ratio of the speed of sound to the ratio of the speed of microwaves (light). One may view the cavity as a temporary artifact that must remain dimensionally stable just long enough to measure  $f_a(p)$  and  $\langle f_m(p) \rangle$  at the temperature  $T$  and that must not change its shape too much when the frequency measurements are repeated at  $T_w$ . (Small, spatially smooth changes in the shape of the cavity affect the frequencies only in the second order of the small change.)

### 3. MEASUREMENTS

In principle,  $u$  (and  $T$ ) could be determined from the frequencies of a single acoustic mode and a single microwave triplet. In this work, as in the redetermination of  $R$ , five non-degenerate acoustic modes spanning the frequency range 2.5 kHz to 9.5 kHz were used. Also, three microwave triplets spanning the frequency range 1.5 GHz to 5.0 GHz were used. The redundant acoustic and microwave measurements helped determine some components of the uncertainty in measuring  $(T - T_{90})$  and also tested the theories for the corrections  $\delta f_a(T)$  and  $\delta f_m(T)$ . We now consider in turn, the measurements of the four variables that appear in Eq. (3):  $f_m, f_a, T$ , and  $p$ .

The microwave resonances had quality factors of more than 5000. The values of  $\langle f_m(T) \rangle$  could be determined very precisely using off-the-shelf instruments and a relatively simple analysis program. The uncertainties of  $\langle f_m(T) + \delta f_m(T) \rangle$  made a negligible contribution to the uncertainty of  $(T - T_{90})$ .

For argon, the acoustic measurements were made on six isotherms: 217.0950 K, 234.3156 K, 253.1500 K, 273.1600 K, 293.1300 K, and 302.9166 K. These measurements spanned the density range  $0.01 \text{ mol}\cdot\text{dm}^{-3}$  to  $0.2 \text{ mol}\cdot\text{dm}^{-3}$ . At these densities, the correction terms in Eq. (3)  $\delta f_a(p, T)$  were small and, in some cases, they tend to cancel out of the ratios in Eq. (3). At low pressures, the contribution to  $\delta f_a(p, T)$  from the thermal boundary layer in the argon where it contacts the shell grows as  $p^{-1/2}$  and the signal-to-noise ratio for measuring  $f_a(T)$  declines as  $p^2$ . At high pressures, the term in  $\delta f_a(p, T)$  from the mechanical response of the shell to the acoustic pressure grows as  $p$  and the terms resulting from the non-ideality of the argon grow as  $p, p^2, \text{ etc.}$  Thus, the argon data were taken over the limited range of intermediate densities where they were most useful for determining  $(T - T_{90})$ .

The acoustic data for xenon were taken on two isotherms: 273.16 K and 302.9166 K. For xenon, the acoustic measurements spanned the density range  $0.014 \text{ mol}\cdot\text{dm}^{-3}$  to  $0.14 \text{ mol}\cdot\text{dm}^{-3}$ . If progressive contamination of the xenon (Section 5, below) had not interfered with the measurements, the xenon data would have been taken to densities as low as  $0.005 \text{ mol}\cdot\text{dm}^{-3}$ .

Three capsule-style standard platinum resistance thermometers were calibrated at the triple points of argon, mercury, water, and gallium, and then installed in the resonator. The uncertainty of the thermometry resulted from the uncertainty of each calibration measurement and from drifts in the system (thermometers + resistance bridge + standard resistor) during the weeks between calibrations. The non-uniqueness of ITS-90 contributed an uncertainty of approximately 0.2 mK to the temperature measurements on the isotherms at 217 K, 253 K, and 293 K. An additional uncertainty resulted from the small temperature difference ( $\approx 0.5$  mK) between the thermometers embedded in the top and bottom of the spherical shell. We estimate that our imperfect knowledge of the volume average of the temperature within the argon was less than 0.1 mK relative to the thermometer calibrations.

We used a calibrated, fused-quartz, bourdon tube gage to measure the pressure of the argon. On the isotherm at 303 K, the worst case,  $u^2$  changes only 0.3% over the range of pressure encountered here. The uncertainty of the pressure measurement made a negligible contribution to the uncertainty of  $(T - T_{90})$ .

### 4. ANALYSIS AND TABULATED RESULTS

The relative uncertainty in the measurement of an acoustic resonance frequency  $f_a(p, T)$  was usually less than  $0.3 \times 10^{-6}$ . With limited and well understood exceptions, the five radially-symmetric acoustic modes yielded consistent results at this level. However, to determine  $T$  and  $(T - T_{90})$  via Eq. (3), we required the  $p60$  limit of the squares of frequency ratios  $[f_a(p, T)/f_a(p, T_w)]^2$ . These limits were determined by fitting multiparameter functions of the pressure to  $f_a(p, T)$ . Because of the correlations among the parameters, the relative uncertainties of the  $p60$  limits ranged from 2.5 to 10 times that of a single measurement of  $f_a(p, T)$ , depending upon functional form chosen and on the isotherm examined. This model-dependence of the  $p60$  limits is the largest contributor to the uncertainty of  $(T - T_{90})$ ; it leads to the "recommended" uncertainties in Table 1 and it is discussed fully in Section 8 of Ref. [1].

Here, we describe two very different analyses of the acoustic data. The first analysis, denoted "isotherm analysis" is one extreme, insofar as it has the most parameters and makes the fewest assumptions concerning the parameters. The results of the isotherm analysis do not have an uncertainty resulting from choosing only one among several competing models for the data. However the isotherm analysis has the largest uncertainties from the correlations among the parameters. The second analysis is denoted "surface analysis" and it imposed as many physically-based constraints on the parameters as possible. Remarkably, the imposition of these constraints changed  $(T - T_{90})$  by

only 0.8 mK in the worst case and only 0.6 mK on average. (See Table 1.) Furthermore, these changes are within the combined uncertainties of the two analyses. In general, imposing more constraints than the isotherm analysis but fewer constraints than the surface analysis led to results and uncertainties between these extreme analyses.

**Table 1.**

$T_{90}/\text{K}$	Isotherm fits ( $T-T_{90}$ )/mK	Surface fit ( $T-T_{90}$ )/mK	<b>Recommended</b> ( $T-T_{90}$ )/mK	Surface fit ( $T-T_{90}$ )/mK
	Argon			Xenon*
<b>302.9166</b>	$3.95 \pm 0.73$	$4.61 \pm 0.33$	<b><math>4.6 \pm 0.6</math></b>	$4.38 \pm 0.66$
<b>293.1300</b>	$2.60 \pm 0.75$	$3.23 \pm 0.31$	<b><math>3.2 \pm 0.6</math></b>	
<b>253.1500</b>	$-2.84 \pm 0.60$	$-2.29 \pm 0.27$	<b><math>-2.3 \pm 0.6</math></b>	
<b>234.3156</b>	$-3.73 \pm 0.60$	$-2.92 \pm 0.19$	<b><math>-2.9 \pm 0.6</math></b>	
<b>217.0950</b>	$-4.03 \pm 0.67$	$-3.55 \pm 0.29$	<b><math>-3.6 \pm 0.6</math></b>	

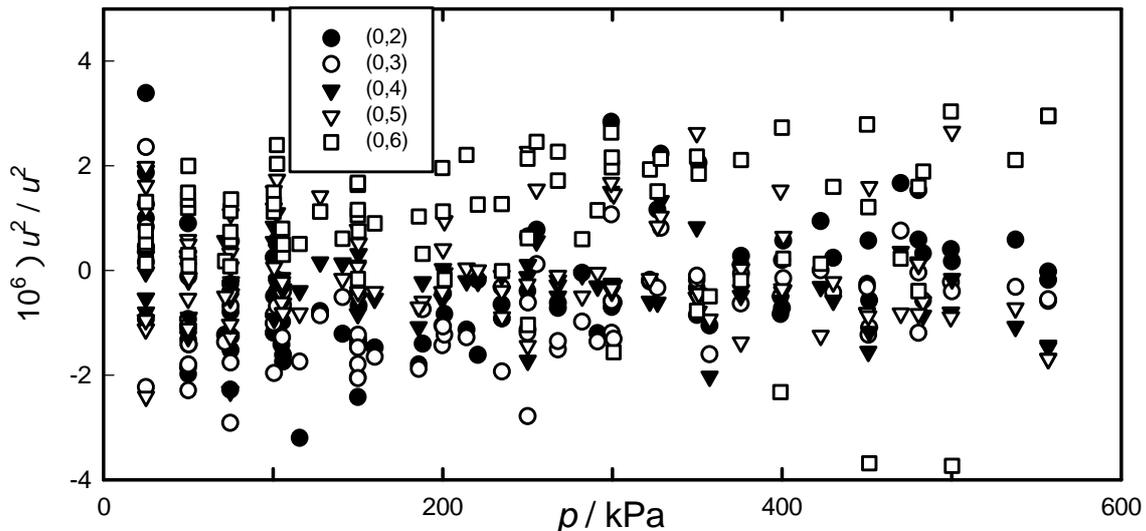
\*For xenon, the uncertainty is the quadrature sum of 0.40 mK from fitting the acoustic data, 0.31 mK from the non-acoustic items, and 0.43 mK from the virtual leak correction.

Table 1 summarizes the present results for ( $T \neq T_{90}$ ) that were obtained using argon and xenon. For the ‘‘isotherm fits,’’ polynomial functions of the pressure  $p$  were fitted to  $u^2(p,T)$  data on each of the five isotherms listed as well as the isotherm 273.16 K. In this analysis, 24 parameters were used to represent the six isotherms comprising the  $u^2(p,T)$  surface. In contrast, the ‘‘surface fit’’ used only 12 parameters. The surface fit was motivated by the observation that all six isotherms are well above the critical temperature of argon ( $1.4 \leq T/T_c \leq 2.0$ ) and well below the critical density ( $D/D_c \leq 0.02$ ). In this region the virial expansion of the equation of state converges rapidly and the virial coefficients have simple temperature dependences. It follows that the coefficients  $A_1(T)$  and  $A_2(T)$  that appear in the pressure expansion

$$u^2(p,T) = A_0(T) + A_1(T)p + A_2(T)p^2 + \dots \quad (4)$$

also have simple temperature dependencies. This observation led to two constraints applying to the temperature range 217 K  $\leq T \leq$  303 K: (1) the difference  $|A_1(T) / A_1(T,\text{expt.}) - A_1(T,\text{calc.})|$  was required to be a (fitted) linear function of  $T$ , and (2), the coefficient  $A_2(T)$  was required to be a (fitted) quadratic function of  $1/T$ . [Here,  $A_1(T,\text{calc.})$  is the prediction from a semi-empirical interatomic potential taken from the literature.] The third constraint was the fixing of the thermal accommodation coefficient  $h$  at its temperature-independent upper bound 1. (See Sec. 8.3 of Ref [1].) With these three constraints, the  $u^2(p,T)$  surface was fitted by 12 parameters.

**Figure 2** Deviations from the 12-parameter surface fit. The various acoustic modes are denoted ‘‘(0,2)’’ etc.



The deviations shown in Fig. (2) do not have obvious dependencies on either temperature or pressure. However, the deviations for the mode (0,6) are larger than those observed for the other modes. (See Fig. 9 of Ref. [1]) If these data had been omitted, the results for ( $T \neq T_{90}$ ) would have changed by less than 0.2 mK.

## 5. ACOUSTIC DATA FOR XENON AND A VIRTUAL LEAK

While the acoustic data for xenon were being acquired at  $T_g$ , we observed a progressive increase of each resonance frequency, even when the xenon was maintained at constant temperature and pressure in the gas-constant resonator. Because there were no known leaks, we attributed the frequency increase to progressive contamination of the xenon from a virtual leak. (A virtual leak is a volume sealed from the laboratory and connected to the resonator by a path of low pumping speed. When such a volume is exposed to a contaminating gas at high pressure, it fills rapidly via Poiseuille flow. Subsequently, it is a long-lived source of contaminants because it can be evacuated only by comparatively slow molecular flow.) A precursor to this problem had been detected during the redetermination of  $R$ . We quote from Ref. [2]: "When the resonator was filled with helium, we measured a slow decrease in the resonance frequencies. In a typical case the fractional decrease was  $9.3 \times 10^{-6} / (100 \text{ h})$  with 438 kPa of He-M in the resonator. . . We speculate that slow desorption of impurities is responsible for these effects. Possible sources of water etc. are the "Viton" O-rings which seal the microphone ports and the fill port to the resonator." To this list of possible sources of contamination, we add the wax used to seal the two hemispheres together.

In order to cope with the progressive contamination of the xenon at  $T_g$ , we measured the resonance frequencies as a function of time  $t$  at each pressure and extrapolated the resulting values of  $f_a(p, T_g, t)$  back to time zero when the resonator was first filled and when, presumably, the contamination began. To reduce the uncertainty of the extrapolation,  $f_a(p, T_g, t)$  was measured at  $T_g$  for three separate fillings of the resonator. In comparison with a single filling, each sample had a shorter residence time and a correspondingly smaller frequency shift. For each sample, we assumed that the contaminant was released at a constant rate  $k$ . The extrapolation procedure was successful. The extrapolated data did not show discontinuities where the samples were changed. The maximum fractional correction to  $u^2$  for the virtual leak was  $7.6 \times 10^{-6}$  (corresponding to 2.3 mK) with an uncertainty of approximately  $0.24 \times 10^{-6}$ . If the correction had been neglected, the value of  $T_g/T_w$  would have been in error by much more than 2.3 mK, in part, because of an incorrect determination of the curvature of the isotherm. Fig. (14) of Ref. [1] shows that the curvature measured during the earlier [3] determination of  $T_g$  is indeed inconsistent with other measurements of the curvature. This supports the conjecture that progressive contamination of the argon used in their work led to an erroneous value of  $T_g$ .

## 6. LESSONS LEARNED

We conjecture that the earlier (1988) determination of  $T_g$  was erroneous, perhaps because of a virtual leak similar to that reported here with xenon. The need to conjecture underlines the most significant deficiency of the gas-constant resonator and the apparatus associated with it: there were no satisfactory provisions for detecting contamination of the gas after it had been admitted into the resonator. Fortunately, all of the results from the gas-constant resonator on the 273.16 K isotherm are mutually consistent; thus, there is no evidence that contamination was a problem during the redetermination of  $R$ .

From our experiences, we recommend 9 improvements to the apparatus and the procedures. To ensure the purity of the thermometric gas, we recommend (1) flowing the gas through the apparatus to reduce its residence time by a factor of 100, thereby reducing its exposure to possible contamination, (2) using a bakeable gas-handling system and transducers (no polymer seals) to minimize sources of contamination, and (3) analyzing the gas exiting the resonator via gas chromatography. A flowing gas system will require (4) tuning the ports that admit gas to the resonator to maintain a high acoustic impedance at the frequencies of the radial resonances while obtaining a low flow impedance to the flow. (A low flow impedance is required to avoid the generation of acoustic noise by turbulence.) For high temperature operation, we recommend (5) simultaneous measurements of acoustic and microwave resonance frequencies to detect possible creep in the resonator's dimensions and (6) positioning the microwave coupling probes to optimize the resolution of the nearly-degenerate microwave resonance frequencies. To improve the thermometry, we recommend (7) installing thermocouples for measuring possible horizontal temperature gradients in the resonator and (8) providing for measurement of the resonator's temperature on ITS-90 with several long-stemmed standard platinum resistance thermometers that can be conveniently inserted and removed from contact with the resonator. (The gas-constant apparatus had to be disassembled to calibrate the thermometers. Thus, extended data runs were precluded by the concern that the thermometers and/or reference resistors might drift between calibrations.) Finally, we recommend (9) extended data runs to acquire data on many, relatively-closely-spaced isotherms. This will permit a more reliable surface analysis of the  $u^2(p, T)$  data. These improvements are being implemented [11]. We anticipate improved primary acoustic thermometry at NIST in the temperature range 217 K to 303 K and up to 800 K.

## ACKNOWLEDGEMENTS

We gratefully acknowledge the full cooperation of the Thermometry Group of NIST including B. W. Mangum, G. F. Strouse, G. T. Furukawa, and D. C. Ripple. J. W. Schmidt of the Pressure and Vacuum Group of NIST calibrated our pressure gauge. The participation of C.W.M. was made possible by an NRC/NBS Postdoctoral Research Associateship. The participation of S.J.B. was possible by the award of a NATO fellowship by the Science and Engineering Research Council (U.K.). The present work builds on the efforts of those who helped develop the gas-constant apparatus and understand its properties. Thus, we thank M. Waxman, M. J. Greenspan, J. B. Mehl, R. S. Davis, T. J. Edwards, J. P. M. Trusler, and M. B. Ewing.

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